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Chlorine-K-x-ray spectra and electronic band structures of $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$

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The $K\beta$-emission and K-absorption spectra of chlorine in $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$ have been obtained with a 50-cm bent-quartz-crystal vacuum spectrograph. The $K\beta$-emission spectra consist of a prominent band $K\beta_1$ and its subbands $K\beta_x$ and $K\beta_5$, although the subbands are ambiguous in $MgCl_2$. Going to the higher-atomic-number-metal chlorides, the half-width of the $K\beta_1$ band decreases and the subband $K\beta_x$ is clearly separated from the $K\beta_1$ band. The $K\beta_1$ band is discussed in relation to the amounts of ionic character of the bond of these chlorides. The subbands $K\beta_x$ and $K\beta_5$ are accounted for in terms of a double-ionization model given by Deslattes. The K-absorption spectra are compared with the Cl $L_{2,3}$-absorption spectra of these chlorides reported previously. A tentative interpretation for the Cl K-absorption and $L_{2,3}$-absorption spectra is made in terms of the core-level-to-band transition. The band gap of these chlorides is estimated.

I. INTRODUCTION

It is well known that the x-ray valence-band emission and absorption spectra of solids give information about the density of states in the valence and conduction bands, respectively. For example, the Cl $K\beta_1$-emission and K-absorption spectra of the alkaline-earth chlorides reflect the distributions of the p-like states in the valence and conduction bands, respectively, and the Cl $L_{2,3}$-absorption spectra reflect the distributions of the s- and d-like states in the conduction band. The Cl $L_{2,3}$-absorption spectra have been investigated by Sato *et al.*[1] (using the synchrotron radiation) and by Saar and Elango[2] (using an x-ray tube). However, the Cl $K\beta$-emission and K-absorption spectra have not yet been reported. Recently, Rabe *et al.*[3] have investigated the Mg^{++} $L_{2,3}$-absorption spectra of MgF_2, $MgCl_2$, and $MgBr_2$ and found sharp absorption bands due to excitons.

In the highly ionic alkaline-earth chlorides[3] the valence band is formed by the $3p$ electrons of the Cl^- ion. The outermost electrons of the alkaline-earth ions are the $2p$ electrons for Mg^{++}, the $3p$ electrons for Ca^{++}, the $4p$ electrons for Sr^{++}, and the $5p$ electrons for Ba^{++}. The binding energies of these electrons in the free atoms are Mg $2p$ 51.4 eV,[4] Ca $3p$ 25.4 eV,[4] Sr $4p$ 19.9 eV,[4] and Ba $5p$ 14.6 eV.[4] The lowest part of the conduction band is formed by the $3s$ state of Mg^{++} for $MgCl_2$, the $4s$ state of Ca^{++} for $CaCl_2$, the $5s$ state of Sr^{++} for $SrCl_2$, and the $6s$ state of Ba^{++} for $BaCl_2$. We suppose that the minimum of the conduction band is at the point Γ at the center of the Brillouin zone and that the symmetry character of the wave functions at this point is of s type. The theoretical band calculation has not yet been made.

The purpose of the present paper is to show the $K\beta$-emission and K-absorption spectra of chlorine in $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$, and to obtain information on the electronic band structure.

II. EXPERIMENTAL

A 50-cm bent-quartz-crystal vacuum spectrograph[5] was used in the present investigation. Both the $K\beta$-emission and the K-absorption spectra were recorded on a Fuji A-1 photographic film in the first-order reflection for the $(11\bar{2}0)$ plane of the crystal. The dispersion of the spectrograph was 3.10 eV/mm on the film.

The starting materials of the alkaline-earth chlorides used here were of the commercial reagent grade and were chemically in the form of $MgCl_2 \cdot 6H_2O$, $CaCl_2 \cdot 2H_2O$, $SrCl_2 \cdot 6H_2O$, and $BaCl_2 \cdot 2H_2O$. These materials were heated in vacuum for several hours to remove water molecules and to obtain powders of $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$.

The emitter for the $K\beta$-emission spectra was powder ($MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$) rubbed onto a tungsten anode of a demountable x-ray tube.[5] Chlorides used here are deliquescent. In order to remove adsorbed water, the sample mounted on the anode was heated in vacuum by the filament of the x-ray tube placed 5 mm from the sample. The operating condition of the x-ray tube was 5 kV and 3 mA. The exposure times were about 15 min.

The absorbing specimens were prepared *in situ* in the form of thin layers evaporated on polypropylene films in a vacuum of 1×10^{-5} Torr. Radiation with a continuous spectrum was obtained from the x-ray tube with a tungsten target, operating at 5.5 kV and 30 mA. The exposure times were about 2 h. The pressure of the spectrograph tank during the experiments was 1×10^{-5} Torr.

Measurements were made on the microphotometer tracings with ×25 magnifications. The results of three individual measurements for each chloride were averaged. The $L\alpha_1$ (2838.61 eV)[6] and $L\alpha_2$ (2833.29 eV)[6] lines of metallic palladium and the Cl $K\beta_1$ line (2815.17 eV)[7] of KCl were used as the reference lines to determine the photon energy values of the $K\beta$-emission and K-absorption spectra of chlorine in the alkaline-earth chlorides.

III. RESULTS AND DISCUSSION

The $K\beta$-emission and K-absorption spectra of chlorine in $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$ are shown in Fig. 1. The photon energy values of the characteristic points in these spectra are given in Table I.

A. Cl $K\beta$-emission spectra

The $K\beta$-emission spectra consist of a prominent band $K\beta_1$ and its subbands $K\beta_x$ and $K\beta_5$, although the presence of the subbands is ambiguous in $MgCl_2$. Going to the higher-atomic-number-metal chlorides, the half-width of the $K\beta_1$ band (which is due to the transition $3p \rightarrow 1s$ within the Cl^- ion) decreases and the subband $K\beta_x$ is clearly separated from the $K\beta_1$ band. This general feature has also been found for the $K\beta$-emission spectra of the Cl^- ion in the alkali chlorides (LiCl,[8] NaCl,[9] KCl, and RbCl[10]), which are shown in Fig. 2. This relates probably with the amounts of ionic character of the bond of these metal chlorides, because the bond in these chlorides is largely ionic and the valence band arises from the $3p$ state of the Cl^- ion. For the alkali chlorides, the alkaline-earth chlorides, and some transition-metal chlorides, the differences in the electronegativity[11] of the metal and chlorine atoms, and the amount[11] of ionic character of the bonds are listed in Table II. When the difference of the electronegativity is larger than 2.0 and the amount of ionic character is larger than 63%, that is, the bond in these chlorides is largely ionic, the $K\beta_1$ band is appreciably narrow and the subband $K\beta_x$ appears to be separated from the $K\beta_1$ band. On the other hand when the difference is smaller than 1.8, that is, these chlorides are largely covalent,

TABLE I. Photon energy values, in eV, of the characteristic points of the $K\beta$-emission and K-absorption spectra of chlorine in $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$.

Notations	$MgCl_2$	$CaCl_2$	$SrCl_2$	$BaCl_2$
$K\beta_1$	2815.3	2815.2	2814.9	2815.2
$K\beta_x$	···	2817.2	2816.8	2817.4
$K\beta_5$	···	2820.9	2820.2	2820.8
A	2825.7	2825.2	2824.2	···
B	2826.7	2826.9	2826.4	2825.3
C	2829.5	2830.4	2830.4	2829.3
D	2835.2	2834.5	2833.1	2833.2
E	2839.6	2840.7	2839.5	2840.6
F	2842.8	···	2842.4	···
G	···	···	2845.2	···

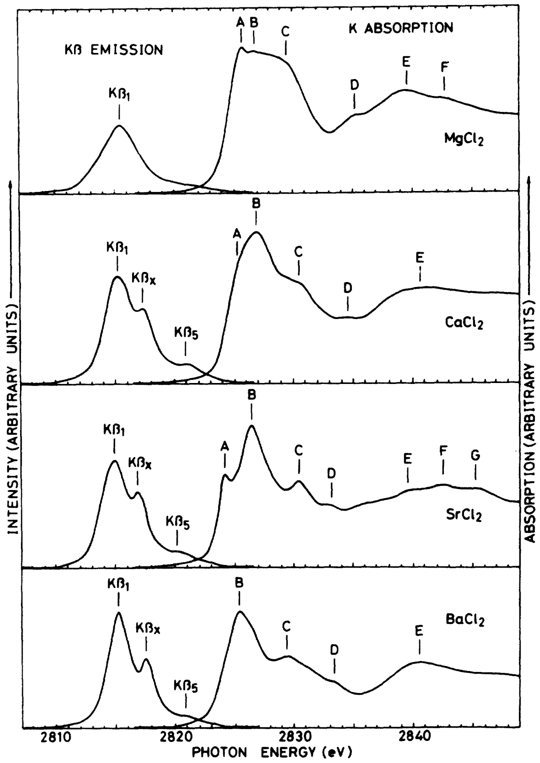

FIG. 1. $K\beta$-emission and K-absorption spectra of chlorine in $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$.

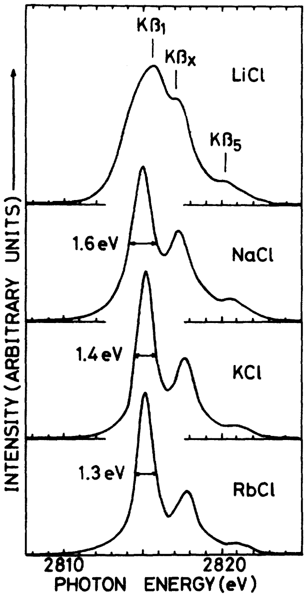

FIG. 2. $K\beta$-emission spectra of Cl^- ion in LiCl (Ref. 8), NaCl (Ref. 9), KCl, and RbCl (Ref. 10).

TABLE II. Relation between electronegativity difference of the metal and chlorine atoms and amount of partial ionic character of single bonds in some metal chlorides (Ref. 11).

Metal chloride	Difference in electronegativity	Amount of ionic character
LiCl	2.0	63%
NaCl	2.1	66
KCl	2.2	70
RbCl	2.2	70
$MgCl_2$	1.8	55
$CaCl_2$	2.0	63
$SrCl_2$	2.0	63
$BaCl_2$	2.1	66
$MnCl_2$	1.5	43
$FeCl_2$	1.2	30
$CoCl_2$	1.2	30
$NiCl_2$	1.2	30

the $K\beta_1$ band is very wide and the $K\beta_x$ band is ambiguous. This spectral feature has also been found for some transition-metal chlorides.[12] Consequently, the width of the $K\beta_1$ band (or the valence band) for these metal chlorides becomes narrow or broad, when the bond is largely ionic or covalent.

Let us consider the subbands $K\beta_x$ and $K\beta_5$. These bands are similar to two satellites $K\beta_x$ and $K\beta_5$ on the high-energy side of the $K\beta_1$-emission band of the Cl^- ion in alkali chlorides (see Fig. 2). These satellites for KCl have been satisfactorily explained by Deslattes[13] using a double-ionization model. Therefore, we compare the subband-$K\beta_1$ separations with the satellite-$K\beta_1$ separations of the Cl^- ion calculated by Deslattes. The energy difference between two peaks $K\beta_1$ and $K\beta_x$ for $BaCl_2$ (or $SrCl_2$ and $CaCl_2$), 2.2 eV, (or 1.9 and 2.0 eV), is in good agreement with the calculated satellite $({}^3P\rightarrow{}^3P,\ {}^1S\rightarrow{}^1P)$ - $K\beta_1$ separations, 2.34, 2.38, 2.45, and 2.50 eV, and the difference between the two peaks $K\beta_1$ and $K\beta_5$, 5.6 eV (or 5.3 and 5.7 eV), also is in good agreement with the satellite $({}^1S\rightarrow{}^3P)-K\beta_1$ separations, 5.14, 5.19, and 5.26 eV. In Fig. 3, the subbands $K\beta_x$ and $K\beta_5$ for $BaCl_2$ are shown together with the locations of the calculated satellite arrays.[13] Consequently, the subbands $K\beta_x$ and $K\beta_5$ for $CaCl_2$, $SrCl_2$, and $BaCl_2$ are probably two satellite complexes arising from double ionization of the Cl^- ion.

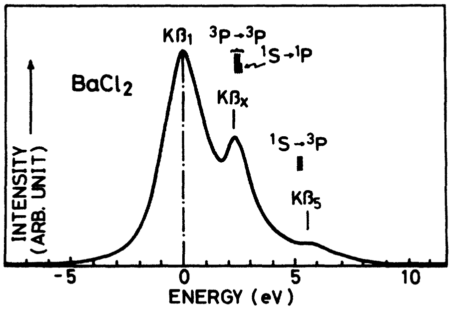

FIG. 3. $K\beta$-emission spectrum of chlorine in $BaCl_2$. The subbands $K\beta_x$ and $K\beta_5$ are assigned in terms of the transition arrays for the Cl^- ion calculated by Deslattes (Ref. 13). The transitions marked with longer vertical lines are expected to have greater intensity than the others.

B. Cl *K*-absorption spectra

The Cl *K*-absorption spectrum of $MgCl_2$ is characterized by the intense and broad band with fine structures *A*, *B*, and *C* and is different from the absorption spectra of $CaCl_2$, $SrCl_2$, and $BaCl_2$, which are somewhat similar to one another except for the first structure *A* (note that the spectrum of $BaCl_2$ does not have the structure *A*). This may be due to the different crystal structures, $MgCl_2$ being of $CdCl_2$ type,[14] $CaCl_2$ of distorted-rutile type,[14] $SrCl_2$ of CaF_2 type,[14] and $BaCl_2$ of $PbCl_2$ type.[14]

Let us now compare the Cl *K*-absorption spectra with the Cl $L_{2,3}$-absorption spectra. In Fig. 4 a comparison of the two absorption spectra for $MgCl_2$ is shown where these two spectra are joined by the photon energy (2622.2 eV)[15] of the Cl $K\alpha_1$ line of $MgCl_2$. The first peak in the $L_{2,3}$ absorption is located at a lower energy than that of the *K* absorption. The general shapes of the two spectra are similar to each other in spite of the different final state in their absorption processes. We here give a tentative interpretation for these spectra in terms

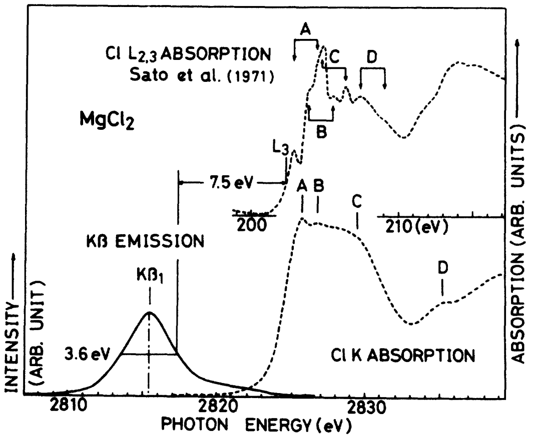

FIG. 4. $K\beta$-emission, *K*-absorption, and $L_{2,3}$-absorption (Ref. 1) spectra of chlorine in $MgCl_2$. The *K* spectra and the $L_{2,3}$-absorption spectrum are joined by the photon energy (2622.2 eV) (Ref. 15) of the Cl $K\alpha_1$ line of $MgCl_2$. The linked arrows in the $L_{2,3}$-absorption spectrum show pairs of peaks arising from the spin-orbit splitting of the $2p$ level of a Cl^- ion and separating by about 1.6 eV. The L_3-absorption edge (202.4 eV) is determined at the midpoint of the edge.

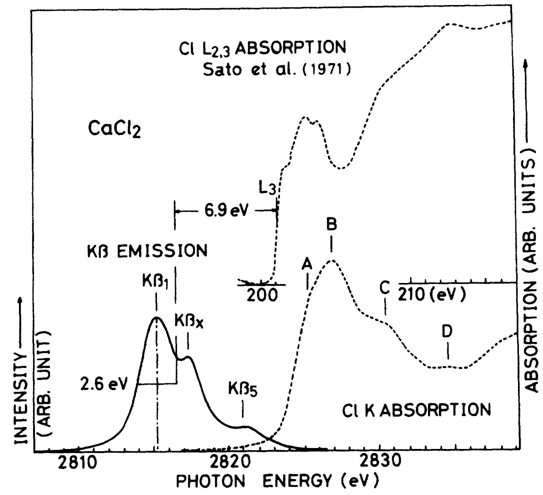

FIG. 5. $K\beta$-emission, K-absorption, and $L_{2,3}$-absorption (Ref. 1) spectra of chlorine in $CaCl_2$. The K spectra and the $L_{2,3}$-absorption spectrum are joined by the photon energy (2622.2 eV) (Ref. 15) of the Cl $K\alpha_1$ line of $CaCl_2$. The L_3-absorption edge (201.2 eV) is determined at the midpoint of the edge.

of the core-level-to-band transition. In the K-absorption spectrum, the first peak A is probably due to the transition to the lowest p-like state (arising from the $3p$ state of the Mg^{++} ion) in the conduction band and the neighboring structures B and C are due to the transitions to the higher-lying p-like states (arising from the $4p$ and $5p$ states of the Cl^- ion and the $4p$ state of the Mg^{++} ion). In the $L_{2,3}$-absorption spectrum the first peaks A [pairs of peaks arising from the spin-orbit splitting (1.6 eV) of the $2p$ level of a Cl^- ion] are due to the transitions to the lowest s-like state (arising from the $3s$ state of the Mg^{++} ion) in the conduction band and the second peaks B are due to the transitions to higher-lying s-like state (arising from the $4s$ state of the Cl^- ion). The third strong peaks C probably correspond to the transitions to the lowest d-like state (arising from the $3d$ state of the Cl^- ion) in the conduction band and the fourth peaks D to higher-lying d-like states. The broad and strong absorption above 211 eV is probably due to the delayed onset[16] of the atomic $2p \rightarrow d$ transition of chlorine. This spectral feature has also been found for the sulfur $L_{2,3}$-absorption spectra of ZnS[17] and CdS.[18]

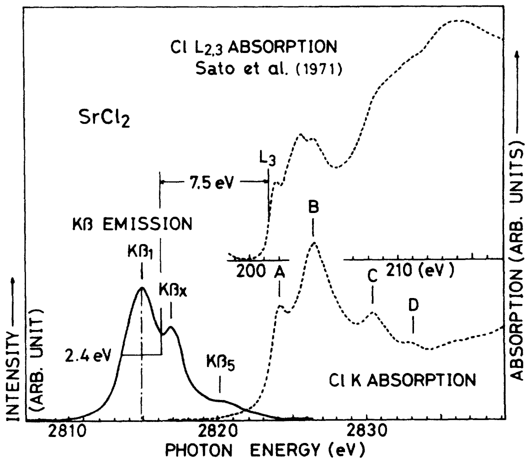

FIG. 6. $K\beta$-emission, K-absorption, and $L_{2,3}$-absorption (Ref. 1) spectra of chlorine in $SrCl_2$. The K spectra and the $L_{2,3}$-absorption spectrum are joined by the photon energy (2622.2 eV) (Ref. 15) of the Cl $K\alpha_1$ line of $SrCl_2$. The L_3-absorption edge (201.4 eV) is determined at the midpoint of the edge.

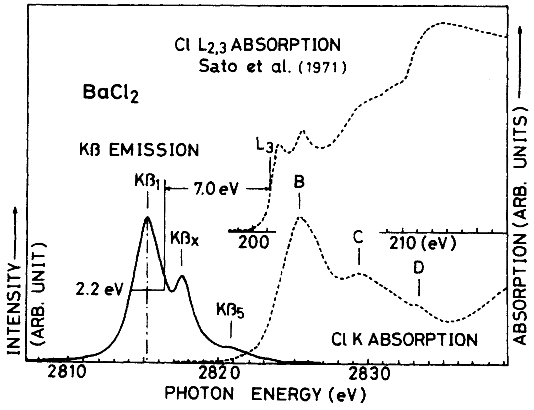

FIG. 7. $K\beta$-emission, K-absorption, and $L_{2,3}$-absorption (Ref. 1) spectra of chlorine in $BaCl_2$. The K spectra and the $L_{2,3}$-absorption spectrum are joined by the photon energy (2622.2 eV) (Ref. 15) of the Cl $K\alpha_1$ line of $BaCl_2$. The L_3-absorption edge (201.1 eV) is determined at the midpoint of the edge.

Figs. 5–7 show a comparison between the Cl K-absorption and $L_{2,3}$-absorption spectra for $CaCl_2$, $SrCl_2$, and $BaCl_2$, respectively. All the $L_{2,3}$-absorption spectra are characterized by the fine structures near the threshold and neighboring intense and broad bands, in contrast with the K-absorption spectra. The first peak in the $L_{2,3}$ absorption is also located at a lower energy than that of the K absorption. In the $L_{2,3}$-absorption spectra, the first peak is due to the transition to the lowest s-like states in the conduction band and the second peak or the third peak (for $CaCl_2$ and $SrCl_2$) is due to the transition to the lowest d-like states. The broad and strong absorption above 205 eV is due to the delayed onset[16] of the atomic $2p \rightarrow d$ transition. In the K-absorption spectra, the first peak A corresponds to the transition to the lowest p-like states (arising from the $4p$ state of the Ca^{++} ion for $CaCl_2$ and the $5p$ state of the Sr^{++} ion for $SrCl_2$) in the conduction band, the second prominent peak B

to the transition to the second low p-like states (arising from the $4p$ state of the Cl^- ion), and the third peak C to higher-lying p-like states. The presence of the first peak A is ambiguous in $BaCl_2$ and only one broad maximum B shows up. This may suggest that the lowest p-like states in the conduction band arise from the overlap of the $6p$ state of the Ba^{++} ion and the $4p$ state of the Cl^- ion.

Let us estimate the band gap of the alkaline-earth chlorides on the basis of the Cl $K\beta_1$-emission band and $L_{2,3}$-absorption spectrum, because the valence band arises from the $3p$ state of the Cl^- ion and the lowest state of the conduction band is the s-like state. If the width of the valence band is given by the experimental half-width of the $K\beta_1$ band and the conduction-band minimum is associated with the L_3-absorption edge (determined at the midpoint of the edge), we can estimate the band gap for $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$ to be 7.5, 6.9, 7.5, and 7.0 eV, respectively (see Figs. 4–7).

IV. CONCLUSION

The $K\beta$-emission and K-absorption spectra of chlorine in $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$ are shown. The $K\beta$-emission spectra consist of a prominent band $K\beta_1$ and its satellites $K\beta_x$ and $K\beta_5$, although the satellites are ambiguous in $MgCl_2$. Going to the higher-atomic-number-metal chlorides, the width of the $K\beta_1$ band (or the valence band) decreases and the satellite $K\beta_x$ is clearly separated from the $K\beta_1$ band. The $K\beta_1$ band is discussed in relation to the amounts of ionic character of the bond of these chlorides. It is confirmed that the bond of $BaCl_2$, $SrCl_2$, and $CaCl_2$ is largely ionic and the bond of $MgCl_2$ is ionic and covalent. The satellites $K\beta_x$ and $K\beta_5$ can be fairly well accounted for in terms of a double-ionization model given by Deslattes. The Cl K-absorption or $L_{2,3}$-absorption spectra may be interpreted from the viewpoint of the core-level–to-band transition. The band gap for $MgCl_2$, $CaCl_2$, $SrCl_2$, and $BaCl_2$ is 7.5, 6.9, 7.5, and 7.0 eV, respectively. It is confirmed that the conduction-band minimum arises from the empty s-like state of the metal ion. Finally we emphasize that theoretical calculation of the electronic energy structure for the alkaline-earth chlorides should be made in order to interpret the chlorine $K\beta$-emission, K-absorption, and $L_{2,3}$-absorption spectra consistently.

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